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Removal of Organophosphonate Herbicide: Adsorption onto Nanosilica †

Violeta-Carolina Niculescu *, Diana Ionela Popescu (Stegarus), Roxana-Elena Ionete and Irina Petreanu

National Research and Development Institute for Cryogenic and Isotopic Technologies—ICSI Ramnicu Valcea, 4th Uzinei Street, 240050 Ramnicu Valcea, Romania

* Correspondence: violeta.niculescu@icsi.ro

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Abstract: Glyphosate (IUPAC name: N-(phosphonomethyl)glycine) is a globally used phosphorous herbicide. Efficient technologies are currently unavailable for glyphosate removal. In this study, nanosilica functionalized with aminopropyl groups was synthesized and studied for glyphosate removal by adsorption. The material was characterized by carrying out SEM, TG, FTIR, BET surface area and pore size distribution measurements. The results showed that the nanosilica was better suited for glyphosate adsorption following the Henry isotherm model, with the reaction being spontaneous and feasible. The performance (quantitative adsorption and complete nanosilica recovery) is worthy of note, considering that the sorbent can be regenerated and reused for at least five cycles.

Keywords: adsorption; herbicides; nanosilica; sustainability

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1. Introduction

Glyphosate represents an organophosphorus broad-spectrum systemic herbicide and crop desiccant that inhibits the plant enzyme 5-enolpyruvylshikimate-3-phosphate synthase [1]. It is the most widely used herbicide to kill weeds, mainly annual broadleaf weeds and grasses that compete with crops. The ecological risks include potential risks to terrestrial and aquatic plants and birds and low toxicity to honeybees. It is frequently detected at low levels in both urban and rural surface waters, or as a residue in food products. Efficient technologies are currently unavailable for total removal [2]. The aim of this study was the synthesis of a nanosilica with improved performance for the total removal of glyphosate herbicide from aqueous solutions.

2. Materials and Methods

The support, nanosilica of SBA-3 type, was prepared using cetyltrimethyl-ammonium bromide and tetraethyl orthosilicate as the template and source of Si, respectively. The obtained silica material was characterized by carrying out SEM, TG, FTIR, BET surface area and pore size distribution measurements. Two solutions of glyphosate in water were prepared. A commercial product containing potassium glyphosate salt-N-(phosphonomethyl) glycine was used. Reactions were monitored by determining total phosphorus and total organic carbon concentration using HACH LANGE LCK 349–350 and HACH LANGE LCK 380–381 kits; concentration readings were performed using a visible HACH DR 3900 spectrophotometer.

3. Results and Discussion

EDS analysis confirmed the percentage of Si. With the introduction of the aminopropyl group, an increase in the percentage of C was observed (due to the propyl groups in 3-aminopropyltriethoxysilane), as well as a high N percentage, indicating amination. SEM revealed almost spherical or spheroidal particles, the particle size being around 50 µm

(Figure 1a,b). The typical FTIR spectra (Figure 1c) showed typical nanosilica adsorption bands: a broad band of asymmetric Si-O-Si stretching vibration at 1050 cm^{-1}; a weak band at 800 cm^{-1} of symmetric stretching vibration for Si-O bonds; and at 3435 cm^{-1}, the support showed a band specific to the presence of OH groups on the surface of silanol groups or from water molecules adsorbed on the surface, its intensity decreasing in amino-SBA-3, demonstrating functionalization. Amino-SBA-3 (Figure 1d) had three ranges of weight loss: 30–115 °C—water loss; 115–330 °C—the fragmentation of aminopropyltriethoxysilane; 330–630 °C—disruption of the remaining mesoporous structure [3,4]. Once the amino groups were introduced, the specific surface area decreased drastically, from 600 m^2/g to 14 m^2/g, and the average pore diameter decreased very little, from 3.8 nm for SBA-3 to 3.2 nm for amino-SBA-3.

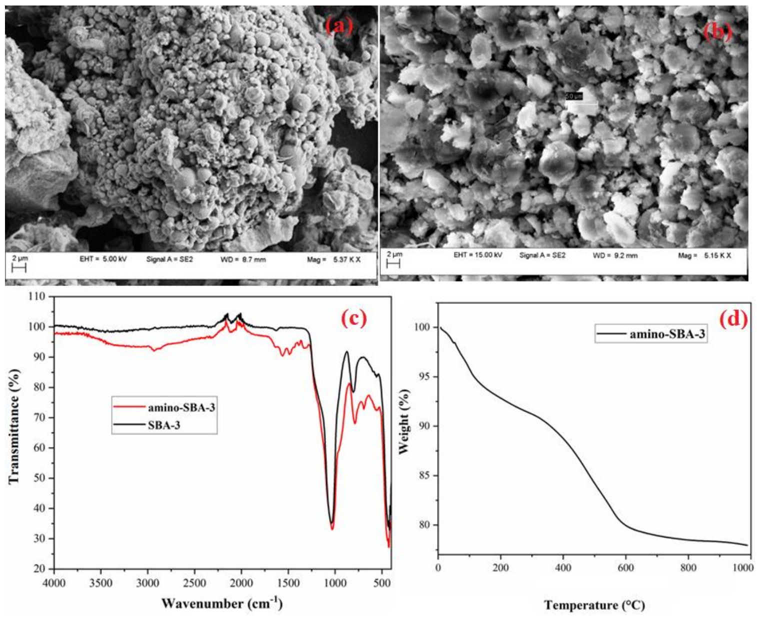

Figure 1. Nanosilica morpho-structural characterization: (**a**,**b**) SEM images; (**c**) FTIR spectra; (**d**) TGA graph.

To evaluate the adsorption properties of the functionalized mesoporous silica, the contact time is an important parameter influencing adsorption. The contact time was in the range 0–120 min. It was observed that the adsorption reached equilibrium after 90 min, defined as the optimal contact time. Since similar values were obtained for the two initial solutions, this study continued using the 0.515 mg/L solution, for which adsorption isotherms were modeled. The values resulting from the analysis of total phosphorus were used (Figure 2). The separation factor of the Langmuir patterns varied between 0.07 and 42.50. Comparing the Langmuir coefficients of determination (R^2), the Langmuir II model reached the highest value (0.985). Comparing the R^2 values of the Langmuir and Henry isotherm models, the highest value (0.995) was obtained for the Henry model, making it the most suitable isotherm describing the adsorption data.

According to the adsorption isotherms, it can be concluded that the adsorption of glyphosate is related to the chemical action between it and mesoporous silica. Considering the chemical structure of the amino-silica surface, bonds are formed between the amino or hydroxyl groups on the mesoporous silica surface as proton donors and the phosphorus atoms in the glyphosate molecules as proton acceptors. In acidic conditions, the surface is positively charged (pH_{zpc} > pH), and glyphosate ions tend to dissociate a proton from the amino groups, due to the electrostatic interaction with the positive surface of the functionalized silica [5]. On the other hand, for the first phosphonate, the hydroxyl bond dissociates with pK_{a1} 0.8, with the interaction taking place between the Si-O-P bond attached to the adsorbent molecules, due to the release of H^+ ions from the oxygen sites [6].

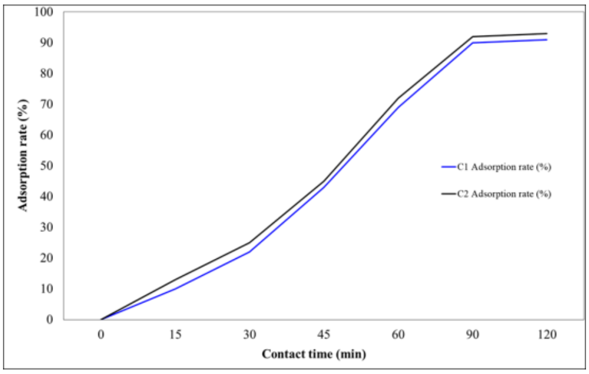

Figure 2. The removal degree as a function of total phosphorus content.

4. Conclusions

This study showed that amino-nanosilica can be used as a suitable adsorbent for the removal of phosphates from aqueous solutions. Quantitative adsorption and complete recovery of the adsorbent were observed. The results showed that the nanosilica was better suited for glyphosate adsorption following the Henry isotherm model and that the reaction was spontaneous and feasible.

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Conflicts of Interest: The authors declare no conflict of interest.

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